



Short communication

Two-step carbon coating of lithium vanadium phosphate as high-rate cathode for lithium-ion batteries

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H I G H L I G H T S

- ▶ A novel carbon-coating method for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ via two-step reaction is presented.
- ▶ The sol–gel and solid-state reaction are combined by using VPO_4 as an intermediate.
- ▶ The end product has a high conductivity of $\sim 10^{-2} \text{ S cm}^{-1}$ with 4.39% residual carbon.
- ▶ Even in 2.5–4.8 V, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode can retain outstanding rate ability.
- ▶ No degradation is found after $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ testing at extreme high rate (120 C).

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Carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was firstly prepared at 850 °C via two-step reaction method combined sol–gel and conventional solid-state synthesis by using VPO_4 /carbon as an intermediate. Two different carbon sources, citric acid and glucose as carbon additives in sequence, ultimately deduced double carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ as a high-rate cathode material. The $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ /carbon with 4.39% residual carbon has a splendid electronic conductivity of $4.76 \times 10^{-2} \text{ S cm}^{-1}$. Even in the voltage window of 2.5–4.8 V, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ /carbon cathode can retain outstanding rate ability (170.4 mAh g^{-1} at 1.2 C, 101.9 mAh g^{-1} at 17 C), and no degradation is found after 120 C current rate. These phenomena show that the two-step carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ can act as a fast charge-discharge cathode material for high-power Li-ion batteries. Furthermore, it's believed that this synthesizing method can be easily transplanted to prepare other lithiated vanadium-based phosphates.

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1. Introduction

Rechargeable lithium battery is regarded as one of the most successful and significant inventions in twentieth century. The appearance of high energy density and high output voltage Li-ion batteries has made the multifunctional portable electronics widely use in our daily life. At the present day, researchers are devoting their great effort to apply the recharge lithium batteries in the fields of energy storage for electric vehicles and the grids [1,2]. For the applications of consumer electronics, the energy density is primary, which has been commendably achieved by using LiCoO_2 [3] or $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ [4] as positive electrodes. The large-scale

energy storage, however, require a long service life and favorable performance with safe condition even in high-current cases. Polyanion-type materials, particularly LiMPO_4 ($\text{M}=\text{Fe}, \text{Mn}$) [5], $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [6], Li_2MSiO_4 ($\text{M}=\text{Fe}, \text{Mn}$) [7], have been discovered as potential cathode candidates for rechargeable lithium batteries in large-scale applications. Nevertheless, splendid capacity is hardly accomplished by this kind of electrodes since the existence of polyanions in their structures.

The lithiated vanadium-based phosphates, such as $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, $\text{Li}_9\text{V}_3(\text{P}_2\text{O}_7)_3(\text{PO}_4)_2$ [8], $\text{Li}_5\text{V}(\text{PO}_4)_2\text{F}_2$ [9], are expected to export more capacity via the multi-electron reaction of vanadium, which can be guaranteed by the Li-rich characteristic within their crystalloid cells [10]. However, the admirable properties of V-based phosphates can't be effortless to attain in the high-power situation on account of their sluggish electron transportation. Doping in V-sites is a popular technique to improve their conductivity, whereas exotic atoms generally suppress the electrochemical activity of

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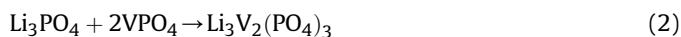
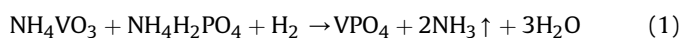
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vanadium to some extent [11]. Carbon coating is still the most effective and straightforward approach to enhance the electronic conductivity and suppress the particle growth [12], which can benefit their rate capability to meet the needs of practical implementations.

Herein, we present a novel carbon-coating method via two-step reaction to synthesize $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$ composite cathode material. The electrochemical performance focused on the rate ability has been investigated on this carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. It is worth to note that, this carbon coating approach presented here may extend the synthesis of other V-based phosphates to improve their rate ability as well.

2. Experimental

Double carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composite has been prepared by two-step synthesis method according to the following reaction scheme



For the first step (1), carbon-coated VPO_4 powders are synthesized via sol–gel method. Stoichiometric amounts of NH_4VO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, and citric acid (half molar magnitude of NH_4VO_3) were employed as the raw materials. Citric acid was added as both chelating reagent and carbon source. First, $\text{NH}_4\text{H}_2\text{PO}_4$ was dissolved in appropriate amount of deionized water. Then, NH_4VO_3 powder was added into the colorless solution with magnetic stirring. Finally, citric acid was added to the solution while stirring until a clear orange solution formed. The solution was heated gently with continuous stirring to remove the excess water at 80°C , and the solution slowly became a sol. The color of the sol changed from green to blackish green during heating process. After drying at 80°C in an air oven over night, the gel was decomposed at 350°C for 5 h in an atmosphere of Ar/H_2 (70/30 in volume percent) in quartz tube furnace to expel H_2O and NH_3 . The precursor was reground for 30 min, and sintered at 900°C for 10 h under the same ambience to obtain crystalline VPO_4 powders. For the second step (2), the preceding VPO_4 powders were mixed with a stoichiometric amount of Li_3PO_4 to get $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Meanwhile, 10% wt. glucose was added into the mixture as the second carbon-coating source. After homogenous ball-milling, the resulting material were calcined at 850°C for another 10 h also in the same ambience to obtain the final product $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$ composite.

The phase identification of VPO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ compounds was carried out by X-ray diffraction (XRD) using a TD-3500 diffractometer from Tongda company with $\text{Cu K}\alpha$ radiation. The indexing analysis of XRD patterns was carried out by using Dicvol-04 program [13]. The carbon content was verified by Vario EL (Elementar, Germany) CHNS elemental analyzer. The electronic conductivity was measured according to linear four-point probe method by using an RTS-8 measurement system.

The electrochemical properties of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$ powders as cathodes in the two-electrode electrochemical cells were measured by using an automatic battery testing system (Land®, China). The cathodes of the cells were fabricated by blending the prepared powder with acetylene black and a polyvinylidene fluoride (PVDF) binder at a weight ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP). The cells were assembled in a Mikrouna glove box filled with high-purity argon, in which lithium metal foil was used as the anode, Celgard® 2320 as the separator and 1M LiPF_6 in EC: DMC (1:1, vol. %) as the electrolyte. The electrochemical capacity measurement was performed in the voltage range of 2.5–4.8 V. The specific capacity was evaluated for the active material only.

3. Results and discussion

The XRD patterns of the intermediate $\text{VPO}_4/\text{carbon}$ and the final product $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$ are shown in Fig. 1. The XRD peaks of the two samples can be indexed by using Dicvol program (Fig. 1), and no other impurities were detected within the resolution of our diffractometer. The indexing results $a = 5.237(1) \text{ \AA}$, $b = 7.785(2) \text{ \AA}$, and $c = 6.289(1) \text{ \AA}$ in orthorhombic system (Cmcm space group) of VPO_4 , and $a = 8.602(8) \text{ \AA}$, $b = 8.592(7) \text{ \AA}$, $c = 12.033(7) \text{ \AA}$, and $\beta = 90.40(8)^\circ$ in monoclinic system ($\text{P}2_1/\text{n}$ space group) of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ agree well with the previous literatures [14,15]. The content of residual carbon is 4.39% in the final product by element analysis, and the carbon should be amorphous since no other peaks attributed to crystalline carbon can be detected in our XRD pattern. The linear four-point probe measurement result shows that the electronic conductivity is $4.76 \times 10^{-2} \text{ S cm}^{-1}$, which is 6 orders of magnitude higher than that of pure $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ ($2 \times 10^{-8} \text{ S cm}^{-1}$) [15], and 1–2 orders of magnitude higher than that of other carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples elsewhere [16,17].

The charge–discharge behaviors of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$ cathode material are tested under various current rates of 0.2 C, 0.5 C, 1.2 C, 2.4 C, 3.5 C, 6.5 C, 17 C, 50 C, and 120 C in the voltage range of 2.5–4.8 V, among which the representative capacity–voltage curves are shown in Fig. 2. The electrochemical behavior at 0.2 C rate, with 185.9 mAh g^{-1} discharge capacity, is well consistent with previously reported result [18]. It exhibits four charge voltage plateaus (3.61 V, 3.69 V, 4.10 V, and 4.56 V) and three discharge voltage plateaus (4.02 V, 3.59 V, 3.52 V) in our experiment, which are relative to a sequence of transition processes between the single phases $\text{Li}_{3-y}\text{V}_2(\text{PO}_4)_3$: $y=0.0, 0.5, 1.0, 2.0$, and 3.0 [15]. Along with the enhancement of charge/discharge rate, the two-plateau boundary becomes ambiguous, and finally disappears in the charge/discharge curves, due to the disordering of Li ions during the extraction/reinsertion process. Meanwhile, the charge plateaus are raised, and the discharge plateaus are declined owing to the voltage polarization caused by the increasing current. Although there are great changes on the charge and discharge profiles, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$ synthesized by two-step reaction here can retain 178.7, 170.4, 157.4, 149, 132.3, 101.9, 64.5, and 32.1 mAh g^{-1} discharge capacity at 0.5 C, 1.2 C, 2.4 C, 3.5 C, 6.5 C, 17 C, 50 C, and 120 C rate, respectively.

Fig. 3 shows the rate ability of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$ at different charge/discharge rates, and finally 1 C in succession. The discharge

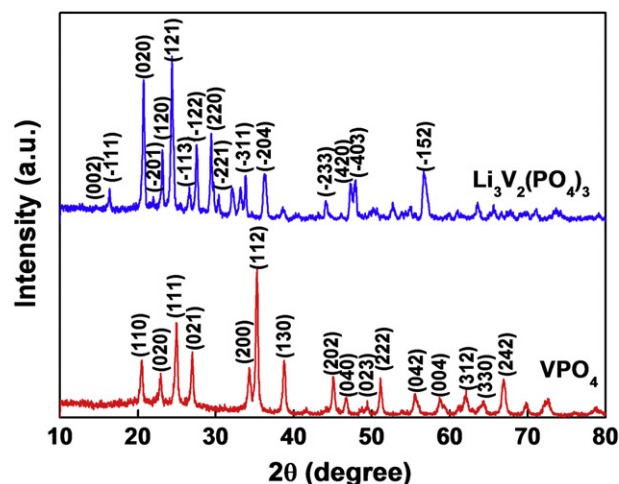


Fig. 1. X-ray diffraction patterns and some representative indexed peaks of the intermediate $\text{VPO}_4/\text{carbon}$ and the final product $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$.

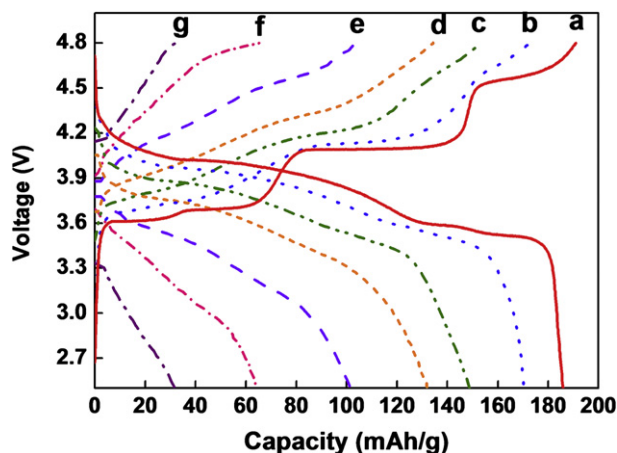


Fig. 2. Charge and discharge curves of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$ positive electrode at (a) 0.2 C, (b) 1.2 C, (c) 3.5 C, (d) 6.5 C, (e) 17 C, (f) 50 C, and (g) 120 C current rates in the voltage window of 2.5–4.8 V.

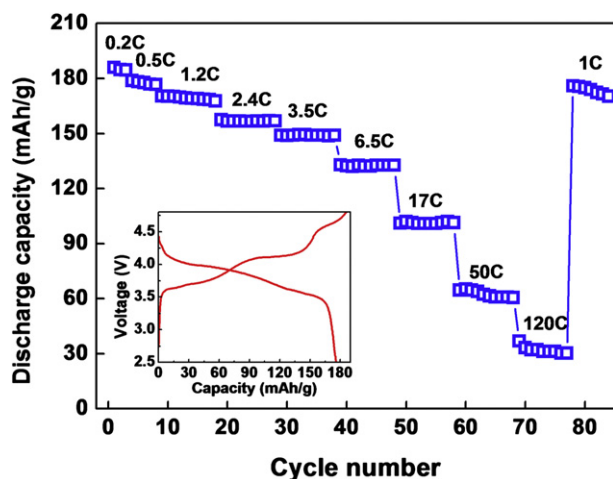


Fig. 3. Rate performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$ cathode material, and (inset) charge-discharge curve of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$ at the final test rate of 1 C.

capacities of each current rate are almost stable within their cycles. The sample can export more than 100 mAh g^{-1} at 17 C rate, namely >50% theoretical capacity can be achieved within 3.5 min. The discharge capacity can retain $\sim 60 \text{ mAh g}^{-1}$ and $\sim 30 \text{ mAh g}^{-1}$ at the rate of 50 C and 120 C, respectively. Recently, many efforts have been made to enhance the rate ability of $\text{Li}_3\text{V}_2(\text{PO}_3)_4$ prepared by different techniques [19–25]. Most of the investigations only focus on the electrochemical performance in the voltage rang of 3.0–4.3 V [19–21], and the rate ability was tested in various discharge rates but charging at the same low rate (0.2 C or 1C) [22,23]. These restrictions are not appropriate to fully evaluate the cathode material, since the $\text{Li}_3\text{V}_2(\text{PO}_3)_4$ can reversibly exact and reinsert the third lithium when the voltage enhances to 4.8 V, and the fast charge ability is also a significant factor for applications. In this work, we found that no evident degeneration is observed even if the batteries charged to 4.8 V and discharged to 2.5 V, and the capacity can be recovered when the rate was back to 1 C. What's more, the charge-discharge curve (inset of Fig. 3) is similar to that of the previous cycle at 1.2 C (Fig. 2c). Furthermore, the rate ability is favorable compared with the results of predecessor researchers

[24,25], even though the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$ here was charged at different high-current rates, which makes it as a potential candidate for the fast-charge energy storage.

4. Conclusion

In this work, a novel carbon-coating method for lithiated vanadium-based phosphates via two-step reaction is presented, and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is an example to corroborate this approach. By using $\text{VPO}_4/\text{carbon}$ as an intermediate product, double carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ can be synthesized at 850°C with citric acid and glucose as carbon additives in sequence. The final product demonstrates a favorable electronic conductivity of $4.76 \times 10^{-2} \text{ S cm}^{-1}$ with only 4.39% residual carbon, which can benefit its energy density. The sample can retain splendid rate ability in a large voltage window (2.5–4.8 V), and no degradation is observed after testing at extreme charge/discharge rate (120 C). After further optimization and amplification on this method, it's believed that the lithiated vanadium-based phosphates, especially $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, can be used as high-power cathode materials in large-scale energy storage.

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